

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

REC'D 21 FEB 2006

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(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 3.41.82256/001	FOR FURTHER ACTION	
See Form PCT/IPEA/416		
International application No. PCT/EP2004/014738	International filing date (day/month/year) 27.12.2004	Priority date (day/month/year) 30.12.2003
International Patent Classification (IPC) or national classification and IPC C08F10/02, C08F2/06, C08F2/14		
Applicant BOREALIS TECHNOLOGY OY et all.		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> <i>(sent to the applicant and to the International Bureau)</i> a total of 2 sheets, as follows:</p> <ul style="list-style-type: none"> <input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). <input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box. <p>b. <input type="checkbox"/> <i>(sent to the International Bureau only)</i> a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <input checked="" type="checkbox"/> Box No. I Basis of the opinion <input type="checkbox"/> Box No. II Priority <input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability <input type="checkbox"/> Box No. IV Lack of unity of invention <input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement <input type="checkbox"/> Box No. VI Certain documents cited <input type="checkbox"/> Box No. VII Certain defects in the international application <input type="checkbox"/> Box No. VIII Certain observations on the international application 		
Date of submission of the demand 31.10.2005	Date of completion of this report 20.02.2006	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Kaumann, E Telephone No. +31 70 340-3640	



INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/014738

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
 - This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
 - international search (under Rules 12.3 and 23.1(b))
 - publication of the international application (under Rule 12.4)
 - international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

Description, Pages

1-19 as originally filed

Claims, Numbers

13(part), 14, 15 as originally filed
1-12, 13(part) received on 01.11.2005 with letter of 31.10.2005

Drawings, Sheets

1/1 as originally filed

- a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. The amendments have resulted in the cancellation of:
 - the description, pages
 - the claims, Nos.
 - the drawings, sheets/figs
 - the sequence listing (*specify*):
 - any table(s) related to sequence listing (*specify*):
4. This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
 - the description, pages
 - the claims, Nos.
 - the drawings, sheets/figs
 - the sequence listing (*specify*):
 - any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-15
	No: Claims	
Inventive step (IS)	Yes: Claims	1-15
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-15
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

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Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Subject-matter

Subject-matter the present application is a process for the (co-) polymerization of ethylene in a slurry or solution phase using a metallocene catalyst system. The diluent is recycled to the hydrogen feed stream. Since the diluent always contains traces of hydrogen, it is avoided that the catalyst comes into contact with the recycled diluent or with hydrogen.

2. Problem and Solution

The technical problem to be solved was to provide a process which avoids the partly deactivation of metallocene catalysts.

This problem is solved by avoiding contact of the catalyst or procatalyst with hydrogen containing recycled diluent or with hydrogen, since hydrogen partly deactivates the metallocene catalyst.

3. Prior Art

Reference is made to the following documents:

D1: WO 96/08520 (cited by the applicant)

D2: WO 00/34341

D3: EP 0 887 379

D4: US 2002/0065376

D1 relates to a gas phase or slurry process for the polymerization of ethylene using a metallocene catalyst system. Page 10, line 16 - 25 discloses that the liquid polymerization medium (which may be a recycle stream) and the ethylene is added to the reactor together with hydrogen and the catalyst.

D2 discloses the metallocene catalyst of the present application, which is used in a gas phase or slurry reactor for the polymerization of ethylene. The catalyst may be prepolymerized and the reaction medium may result from a previous reaction step. A gas phase step can follow. In one embodiment the feed of the first reactor can consist of the reaction mixture from a previous reactor, together with added fresh monomer, optional

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hydrogen and/or comonomer and cocatalyst.

D3 discloses a process for the polymerization of propylene using a metallocene catalyst (see col. 9, line 43 to col. 10, line 1). The process comprises a prepolymerization step, a slurry main polymerization step followed by a gas phase polymerization. In one embodiment (see col. 14, lines 6 - 21), a monomer containing stream is recycled back to the reactor. The stream may also contain hydrogen and catalyst.

D4 discloses a slurry process for the polymerization and copolymerization of ethylene, comprising a prepolymerized metallocene catalyst and hydrogen as molecular weight regulator, which is added along with the catalyst (see [0100]).

4. Article 33(2) PCT (Novelty)

The process according to **claims 1 - 15** appears to be novel.

5. Article 33(3) PCT (Inventive Step)

Contrary to the disclosures of the available prior art, the claimed process for the (co-)polymerization of ethylene in a slurry or solution phase, using a metallocene catalyst system, avoids that the catalyst comes into contact with the recycled diluent which may contain hydrogen, or directly with hydrogen.

The technical effect thereof is that a deactivation of the catalyst by hydrogen is avoided. The examples and comparative examples, whereon the shown technical effect is based, compare catalysts, which have not been precontacted with hydrogen to catalysts, which have been precontacted with hydrogen.

Hydrogen is normally used in polymerization reactions as molecular weight regulating agent. It appears that a negative effect of hydrogen on the catalyst activity was not considered in the art.

Therefore, it appears that the present inventors have described a surprising technical effect.

Therefore, an inventive step can be acknowledged.

6. Article 33(4) PCT (Industrial Applicability)

Since a high catalyst activity in solution and slurry process for the polymerization of ethylene is of very industrial interest, industrial applicability can be acknowledged.

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Claims

01. 11. 2005

1. A process for the polymerisation of ethylene or ethylene and at least one C_{3-20} alpha olefin comonomer in the slurry or solution phase in a reactor having a polymer outlet stream, a procatalyst or catalyst feed stream and a hydrogen feed stream, said polymerisation being effected in the presence of a metallocene catalyst, a diluent and hydrogen, characterised in that said diluent is recycled from said outlet stream to said hydrogen feed stream, said procatalyst or catalyst feed stream is free of hydrogen, said hydrogen feed stream is free of procatalyst or catalyst and said procatalyst or catalyst feed stream does not comprise recycled diluent.

15 2. A process as claimed in claim 1 wherein the metallocene catalyst is fed to the reactor.

3. A process as claimed in claim 1 or 2 wherein said process takes place in the slurry phase.

20 4. A process as claimed in claim 1 to 3 wherein said diluent is propane, n-butane or isobutane.

25 5. A process as claimed in any one of claims 1 to 4 wherein said metallocene catalyst is supported.

6. A process as claimed in any one of claims 1 to 5 wherein said comonomer is butene, octene or hexene.

30 7. A process as claimed in any one of claims 1 to 6 further comprising a gas phase polymerisation stage subsequent to said slurry or solution polymerisation.

35 8. A process as claimed in any preceding claim wherein said metallocene catalyst is prepolymerised.

9. A process as claimed in any one of claims 1 to 8 wherein said catalyst feed stream comprises a catalyst feed vessel in which said metallocene catalyst is resident for at least 2 hours.

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10. A process as claimed in any preceding claim wherein prior to said process a Ziegler-Natta catalysed polymerisation is effected.

10 11. A process as claimed in claim 10 wherein the change from Ziegler-Natta to metallocene catalysis is effected continuously (i.e. without reactor shutdown) by stopping the feed of Ziegler-Natta catalyst feed and starting metallocene catalyst feed to the reactor.

15 12. A process as claimed in any one of claims 1 to 11 wherein said metallocene catalyst comprises a compound of formula

20 $Cp',_2MX',_2$

wherein M is a group 3 to 10 transition metal, each X' is halogen, diC_{1-6} -alkylamido, C_{1-6} alkyl, benzyl or hydrogen;

25 each Cp' is an unsubstituted cyclopentadienyl or indenyl group or a cyclopentadienyl or indenyl group substituted by one or more groups selected from C_{1-10} hydrocarbyl or siloxy, said Cp' groups being bridged or not bridged.

30 13. A process for the polymerisation of ethylene or ethylene and at least one C_{3-20} alpha olefin comonomer in the slurry phase or solution phase in a polymerisation reactor comprising the steps of:

35 continuously introducing ethylene and optionally at least one C_{3-20} alpha olefin comonomer into said reactor; continuously introducing diluent into said reactor;